

Degradation of Diuron Photoinduced by Iron(III) in Aqueous Solution

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Abstract: The degradation of diuron photoinduced by iron(III) in aqueous solution has been investigated with different iron(III) species (monomeric species $\text{Fe}(\text{OH})^{2+}$, dimeric species $\text{Fe}_2(\text{OH})_2^{4+}$ and water-soluble oligomeric species) under monochromatic excitation at 365 nm and under sunlight. The rate of degradation depends on the concentration in $\text{Fe}(\text{OH})^{2+}$, the most reactive species in terms of $\cdot\text{OH}$ radical formation. The major photoproduct is 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea which represents more than 60% of diuron disappearance. The mechanism only involves the attack by $\cdot\text{OH}$ radicals arising from iron(III) excited species. The half-lives of diuron when submitted to such a process in the environment were estimated to be 1–2 h and a few days according to the concentration of $\text{Fe}(\text{OH})^{2+}$ (respectively 70% and <10% of total iron(III) concentration).

Key words: iron(III), diuron, photodegradation, aqueous solution, hydroxy radicals

1 INTRODUCTION

The contamination of aquatic bodies by potentially harmful organic chemicals is one of the great environmental problems. Among the molecules used in agriculture, diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) is widely used as herbicide because of its inhibition of photosynthesis. As a result it is found in water bodies.^{1,2} Because its herbicidal activity is required during seed germination, diuron biodegradation has to be very slow and photochemistry with sunlight can provide an alternative way for the degradation of the pollutant to occur. In addition, it has been proved that the photodegradation of organic molecules in aqueous solution is accelerated by the presence of dissolved iron(III) species.^{3,4} This phenomenon is related, firstly, to the fact that organic molecules do not significantly absorb solar light, whereas iron(III) in aqueous solution does absorb, and, secondly, that the photoredox process taking place upon excitation of iron(III) in aqueous

solution gives rise to iron(II) and $\cdot\text{OH}$ radicals.^{5,6} $\cdot\text{OH}$ radicals are known to be very active species, able to oxidize most organic substrates. The simultaneous reoxidation of iron(II) into iron(III) by oxygen confers a catalytic aspect to the process.⁷

In this work, we investigated the degradation of diuron photoinduced by iron(III) in aqueous solution. The study of the process in well-controlled situations in terms of excitation wavelength, pH and iron(III) speciation enabled us to estimate the half-life of diuron in the environment when it undergoes this process. Photodegradation of diuron under solar light in the presence of iron(III) was also performed.

2 EXPERIMENTAL

2.1 Materials

Ferric perchlorate nonahydrate ($\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$; >97%) was purchased from Fluka and used without further purification. Diuron was a Rhône Poulenc Agrochimie product, technical grade, used without purification. Isopropanol was a Prolabo product (HPLC

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grade Chromanorm 99.7%). Solutions were prepared with ultra-pure water (Millipore α Q). The ionic strength was not controlled and pH measurements were carried out with an Orion pH meter to 0.01 pH units. Deaerated solutions were obtained by bubbling with argon for 40 minutes at room temperature.

2.2 Apparatus

2.2.1 Irradiation at 365 nm

The irradiation set-up was a cylinder made of stainless steel, built upon an elliptical base. A high-pressure mercury lamp (Mazda MAW Type 125 W), the emission of which at 365 nm was selected by an inner filter ('black light'), was located at a focal axis of the elliptical cylinder, and the reactor, a water-jacketed Pyrex tube, was centred at the other focal axis. The reaction medium was stirred. The absorbed light intensity measured by ferrioxalate actinometry was $I_a = 4.0 \times 10^{15}$ photons $\text{sec}^{-1} \text{ cm}^{-3}$ for an irradiated volume of 50 cm^3 .⁸

2.2.2 Irradiation at 313 nm

A high-pressure mercury lamp with a Bausch and Lomb monochromator was used for irradiation at 313 nm. The beam was parallel and the reactor was a square quartz cuvette with a 1 cm pathlength. The incident light intensity measured by ferrioxalate actinometry was $I_0 = 7.8 \times 10^{14}$ photon $\text{sec}^{-1} \text{ cm}^{-2}$.

2.3 Analysis

UV-visible spectra were recorded on a Cary 3 double beam spectrophotometer. HPLC experiments were carried out using a Beckman 420 chromatograph equipped with a UV detector Beckman 163 or a Waters 540 system equipped with a photodiode array detector Waters 990. The eluent was methanol + water (60 + 40 by volume) acidified by phosphoric acid (1.8 g litre^{-1}). The flow rate was 1 ml min^{-1} and the column was a Merck Lichrospher 100 RP 18 (5 μm) of 25 cm length.

The percentage of iron(III) monomeric species in iron(III) solution, $\text{Fe}(\text{OH})^{2+}$ in our experimental conditions, was continuously decreasing; the decrease was fast at the beginning and slowed down with ageing of the solution. Iron(III) monomeric species concentration was determined by complexometry with 8-hydroxyquinoline-5-sulfonic acid (HQSA). The absorbance of the resulting complex $\text{Fe}(\text{HQS})_3$ was monitored at 572 nm as described by Faust and Hoigné.⁵ Iron(II) concentration was determined by complexometry with orthophenanthroline. Diuron degradation and photo-products formation were followed by HPLC (UV detection at 250 nm) by measuring the areas of the corresponding peaks.

3 RESULTS

3.1 Iron(III) and diuron in aqueous solution

Under our experimental conditions ($\text{pH} = 3.35$), iron(III) mainly exists as monomeric species $\text{Fe}(\text{OH})^{2+}$ and dimeric species $\text{Fe}_2(\text{OH})_2^{4+}$; water molecules coordinating to iron(III) are omitted.

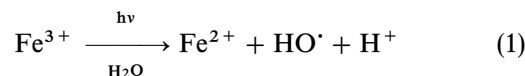
Diuron is only slightly soluble in water with a maximum of solubility of around 0.18 mM .¹ We worked with 0.050 mM diuron solution. The UV-visible spectrum of diuron in aqueous solution presents two absorption bands at $\lambda = 210 \text{ nm}$ ($\epsilon = 21\,800 \text{ M}^{-1} \text{ cm}^{-1}$) and $\lambda = 247 \text{ nm}$ ($\epsilon = 13\,400 \text{ M}^{-1} \text{ cm}^{-1}$) and a plateau at around 285 nm ($\epsilon \approx 800 \text{ M}^{-1} \text{ cm}^{-1}$). There is no more absorption at $\lambda > 310 \text{ nm}$.

In Fig. 1 are represented the UV-visible spectra of the two iron(III) species: $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}_2(\text{OH})_2^{4+}$ together with the solar light intensity.^{5,10} There is a shift of λ_{max} from 297 nm ($\epsilon = 2030 \text{ M}^{-1} \text{ cm}^{-1}$) to 335 nm ($\epsilon = 5000 \text{ M}^{-1} \text{ cm}^{-1}$) when going from the monomeric species $\text{Fe}(\text{OH})^{2+}$ to the dimeric species $\text{Fe}_2(\text{OH})_2^{4+}$, the dimeric form presenting a higher absorption and at longer wavelength than the monomeric species $\text{Fe}(\text{OH})^{2+}$. There is a significant overlap between the two spectra of iron(III) species and the solar emission. This overlap allows iron(III) species to undergo a photolysis process in the environment.

When iron(III) (0.20 mM) and diuron (0.050 mM) were mixed together ($\text{pH} 3.35$: natural pH of the mixture), the resulting UV-visible spectrum was the sum of UV spectra of the components: there was no detectable complexation in the ground state. The solution was stable in the dark; there was neither redox reaction nor precipitation at least within a few days.

3.2 Photochemical behavior

Upon irradiation at $\lambda > 300 \text{ nm}$, iron(III) species (monomeric and dimeric) are known to undergo a redox process giving rise to iron(II) and $\cdot\text{OH}$ radicals (reaction 1).



The quantum yield that measures the efficiency of reaction (1), i.e. the efficiency of one photon to form one iron(II) and one $\cdot\text{OH}$ radical strongly depends on the nature of iron(III) species.^{5,10} The monomeric species $\text{Fe}(\text{OH})^{2+}$ appears to be the more reactive species in terms of $\cdot\text{OH}$ radical formation. Moreover, the quantum yield is also affected by the excitation wavelength. The photochemical features of the monomeric species, the dimeric species and iron(III) solutions containing different $\text{Fe}(\text{OH})^{2+}$ percentages are gathered in Table 1.

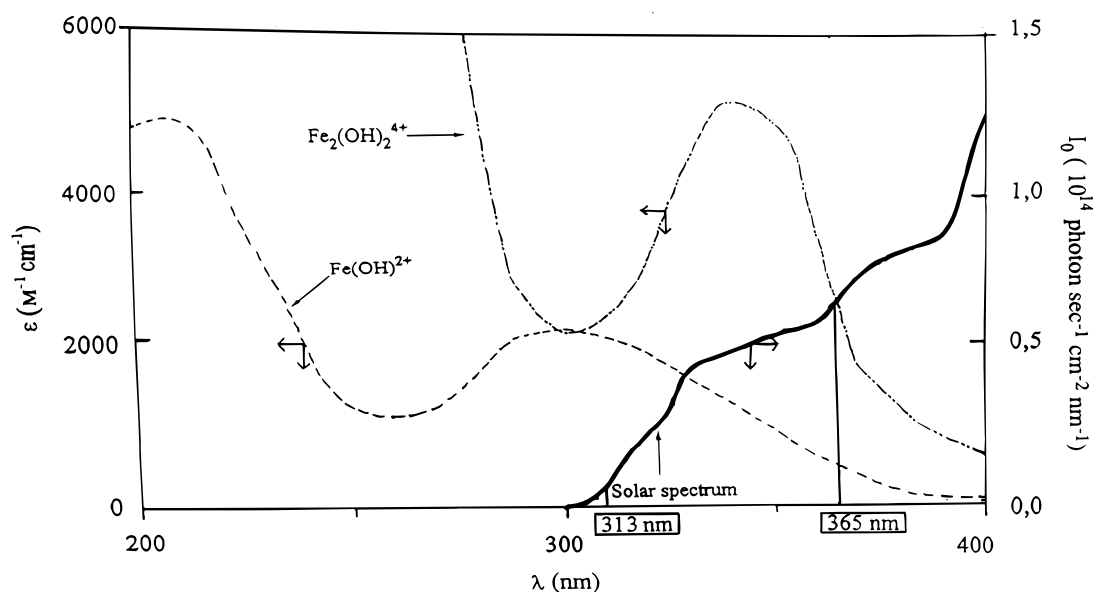


Fig. 1. UV-visible spectra of $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}_2(\text{OH})_2^{4+}$ and solar spectrum in June 1988.

Accordingly, the percentage in $\text{Fe}(\text{OH})^{2+}$ was an important parameter in the system, the concentration of the dimeric species being negligible.⁵

Since there was a continuous thermal evolution,⁹ the concentration in $\text{Fe}(\text{OH})^{2+}$ was systematically measured before irradiation as described in the experimental section.

$$\% \text{Fe}(\text{OH})^{2+} = \frac{[\text{Fe}(\text{OH})^{2+}]}{[\text{iron(III)}]_{\text{tot.}}} \times 100$$

When the mixture was irradiated at 365 nm, a decrease in absorbance was observed all across the spectrum (Fig. 2); iron(III) and diuron disappeared upon irradiation. Iron(III) was reduced to iron(II) according to eqn (1); iron(II) formation was measured by complexometry. Diuron disappearance was followed

by HPLC. Figure 3 shows the diuron disappearance upon irradiation of an iron(III)–diuron mixture containing different percentages of monomer $\text{Fe}(\text{OH})^{2+}$ (70–50%) and less than 5% of a constant total concentration in iron(III) in the solution (0–20 mM). The rate of diuron degradation was divided by a factor of about 100 when the percentage of monomer went down from 70% to a value lower than 5%. The kinetics of diuron disappearance appeared to be first-order (Fig. 4) whatever the percentage of $\text{Fe}(\text{OH})^{2+}$ in the iron(III) solution. The rate constants are collected in Table 2. In order to be able to compare the apparent efficiency of the photons for the different percentages, a pseudo value of quantum yield of diuron disappearance was also calculated by dividing the rate of disappearance by the number of photons absorbed by the solution in one second (Table 3). The formation of iron(II) was also strongly affected by the percentage of $\text{Fe}(\text{OH})^{2+}$ (Fig. 5). The quantum yield of iron(II) formation was not significantly affected by the presence of diuron. The ratio between the quantum yields of iron(II) formation and between the pseudo quantum yields of diuron disappearance upon irradiation of solutions containing a quite different percentage of monomer $\text{Fe}(\text{OH})^{2+}$ (70% and less than 5%) was roughly constant (200 to 260)

TABLE 1
Photochemical Features of Iron(III) Species and Iron(III) Solutions

Species	Percentage (%)	$\phi \text{ Fe}^{II} \text{ form}$	$\lambda_{\text{exc}} \text{ (nm)}$
$\text{Fe}(\text{OH})^{2+}$	100 ^a	0.14	313
		0.017	360
$\text{Fe}_2(\text{OH})_2^{4+}$	100 ^a	0.007	350
$\text{Fe}(\text{OH})^{2+}$	90 ^b	0.08	313
		0.055	365
$\text{Fe}(\text{OH})^{2+}$	11 ^b	0.02	313
		0.008	365

^a Ref. 5.

^b This work.

TABLE 2
First-Order Apparent Rate Constants for Diuron Degradation

$\text{Fe}(\text{OH})^{2+} \text{ (%)}$	$k_{\text{app}} \text{ (min}^{-1}\text{)}$
70	96×10^{-4}
50	25×10^{-4}
<5	0.66×10^{-4}

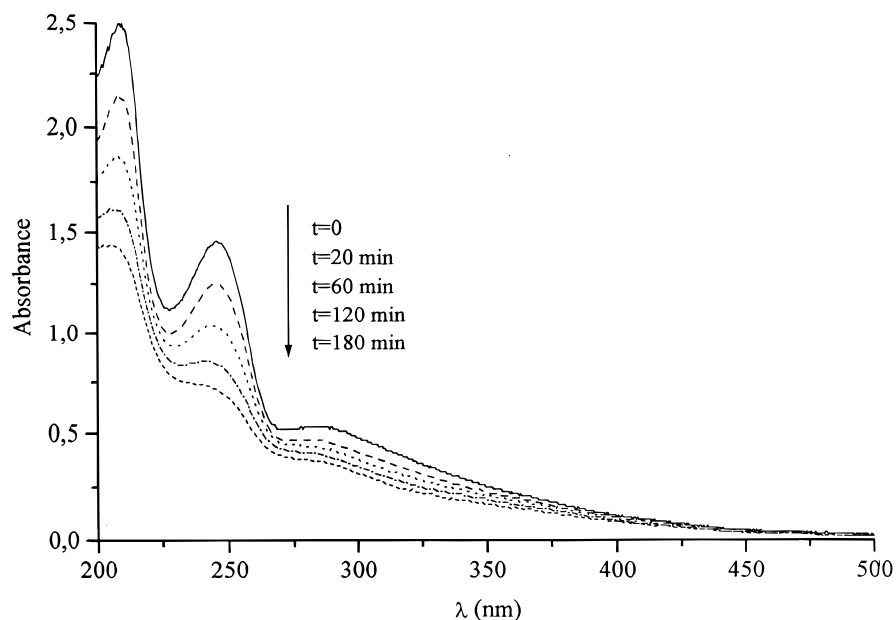


Fig. 2. Spectral evolution of a mixture of $[\text{iron(III)}] = 0.20 \text{ mM}$ with 70% of Fe(OH)^{2+} and $[\text{diuron}] = 0.050 \text{ mM}$ upon irradiation at 365 nm.

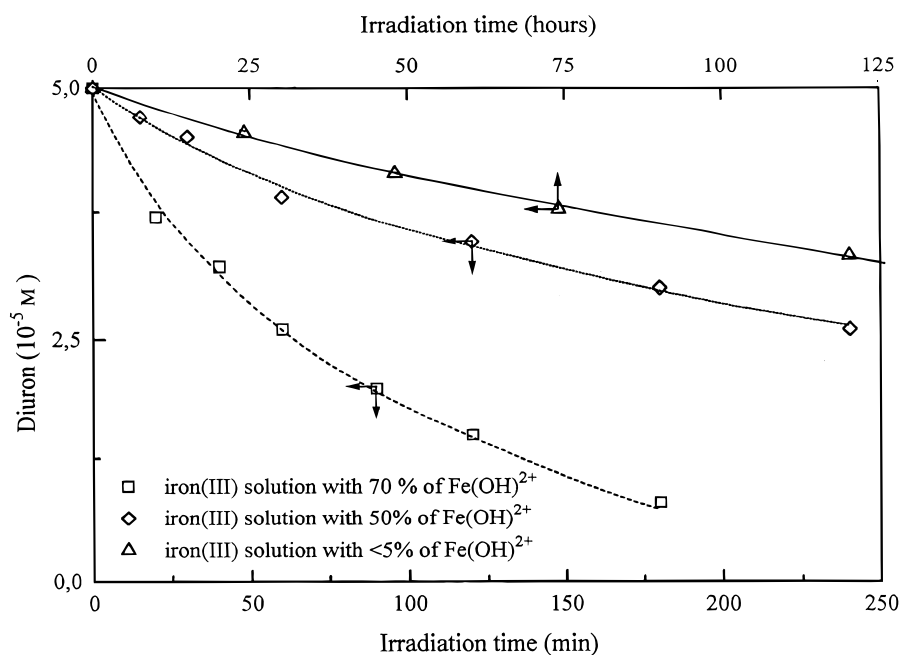


Fig. 3. Kinetics of diuron disappearance upon irradiation at 365 nm with different percentages of monomeric species in the iron(III) solution.

TABLE 3
Quantum Yields upon Excitation at 365 nm

	Monomer (%)			$R = (\phi_{70\%}/\phi_{<5\%})$
	70	50	<5	
Fe(OH)^{2+}				
ϕ' diuron dis.	6.5×10^{-3}	1.0×10^{-3}	2.5×10^{-5}	260
ϕ Fe^{II} form.	2.6×10^{-2}	1.0×10^{-2}	1.3×10^{-4}	200

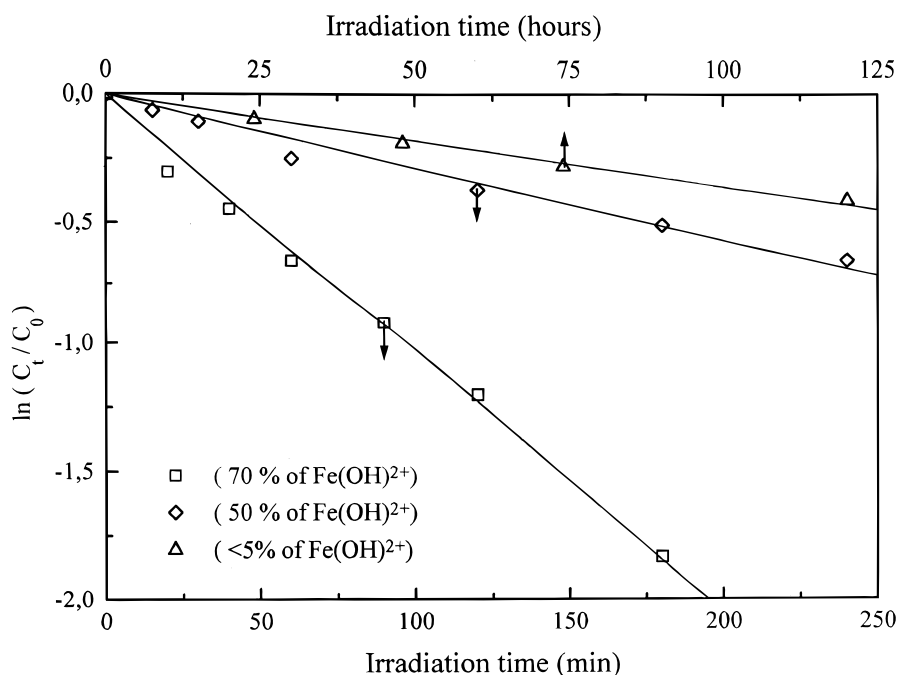


Fig. 4. First-order linearisation of diuron disappearance for different percentages of monomeric species in the iron(III) solution.

(Table 3). The quantum yield of iron(II) formation was always higher than that of diuron disappearance, implying some subsequent thermal reaction giving rise to additional iron(II) (Table 3).

The pseudo quantum yields of diuron disappearance ' ϕ ' were also measured upon irradiation at 313 nm again with two different percentages of monomeric form:

$$[\text{iron(III)}] = 0.20 \text{ mM}$$

$$[\text{Diuron}] = 0.050 \text{ mM}$$

$$\times \begin{cases} 70\% \text{ of } \text{Fe}(\text{OH})^{2+} \text{ '}\phi\text{' diuron dis.} = 5.0 \times 10^{-2} \\ <10\% \text{ of } \text{Fe}(\text{OH})^{2+} \text{ '}\phi\text{' diuron dis.} = 1.6 \times 10^{-4} \end{cases}$$

In all cases, the complete degradation of diuron was observed.

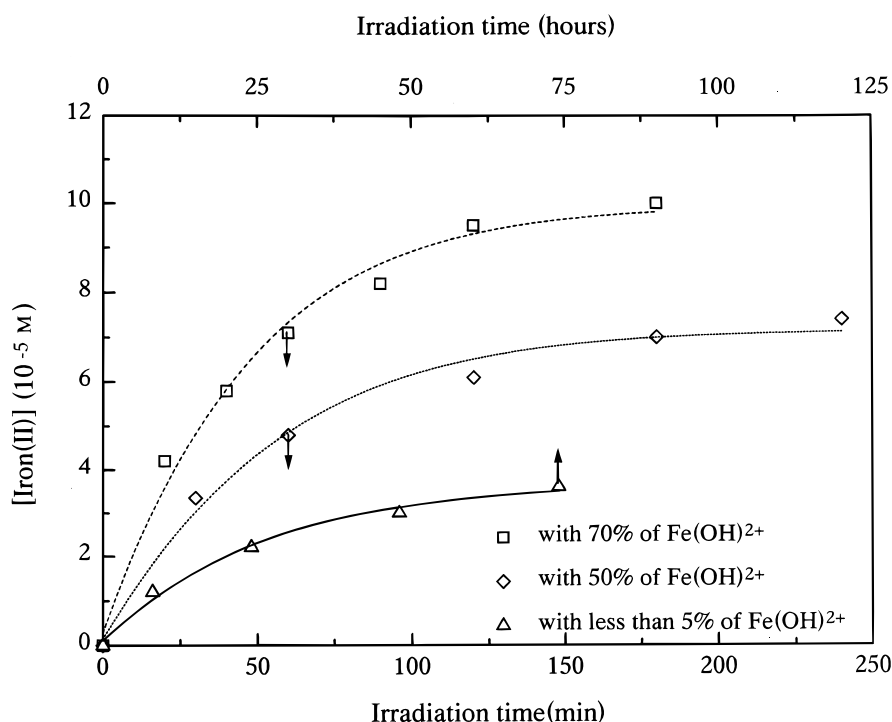


Fig. 5. Kinetics of iron(II) formation upon irradiation at 365 nm with different percentages of monomeric species in the iron(III) solution.

In the absence of oxygen and upon irradiation at 365 nm, the formation of iron(II) was slowed down by a factor of two, but the disappearance of diuron was almost completely inhibited, the degradation only being detectable by the presence of traces of hydroxylated photoproducts.

When irradiated at 365 nm in the presence of isopropanol used as a scavenger of $\cdot\text{OH}$ radicals, there was no degradation of diuron, whereas a significant formation of iron(II) was observed.

3.3 Identification of the photoproducts

Several peaks appeared in the HPLC chromatogram of an irradiated mixture (Fig. 6). The main photoproducts were identified (see Table 4). The products of hydroxylation of the aromatic ring 1 and 2 were detected near the injection peak. These two compounds have been already observed by Tanaka *et al.*¹¹ who investigated the direct photolysis of diuron under ultraviolet excitation.

The major photoproduct 3 was identified from the NMR and mass spectra:

$$\text{MS: main peak: } \frac{m}{e} = 246$$

^1H NMR (CD_3OD):

$$\begin{cases} \delta 3.00 \text{ (s, 3H)} \\ \delta 7.40 \text{ (dd, 1H, } J_1 = 9 \text{ Hz, } J_2 = 2.5 \text{ Hz)} \\ \delta 7.55 \text{ (d, 1H, } J_1 = 9 \text{ Hz)} \\ \delta 7.92 \text{ (d, 1H, } J_1 = 2.5 \text{ Hz)} \\ \delta 9.40 \text{ (s, 1H)} \end{cases}$$

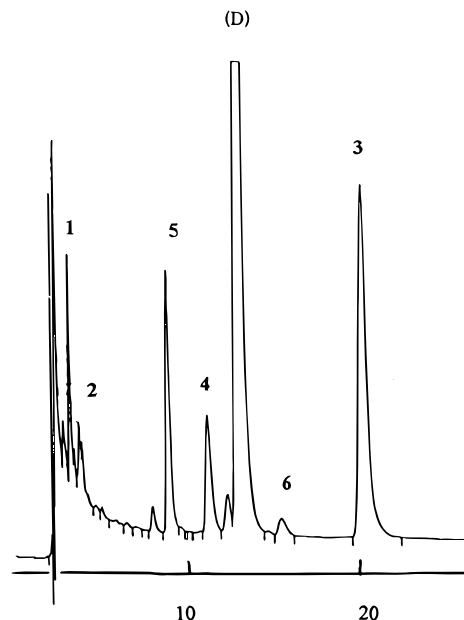


Fig. 6. HPLC chromatogram of a mixture of $[\text{iron(III)}] = 0.20 \text{ mM}$ with 70% Fe(OH)^{2+} and $[\text{diuron}] = 0.050 \text{ mM}$, irradiated 90 min at 365 nm. (D): diuron, 1 ... 6: photoproducts. Detection: $\lambda = 250 \text{ nm}$, Eluant: methanol + water (60 + 40 by volume) + phosphoric acid (1.8 g litre^{-1}).

Its concentration was measured by calibration with an authentic sample synthesized in SEESIB Laboratory by analogy with Crosby's procedure related to monuron.¹² It represents at least 60% of diuron disappearance (Fig. 7). The same adapted procedure was used to synthesize photoproduct 4. The secondary photoproducts 5 and 6 were isolated and identified by mass spectrometry,¹³ each of them accounting for about 5%

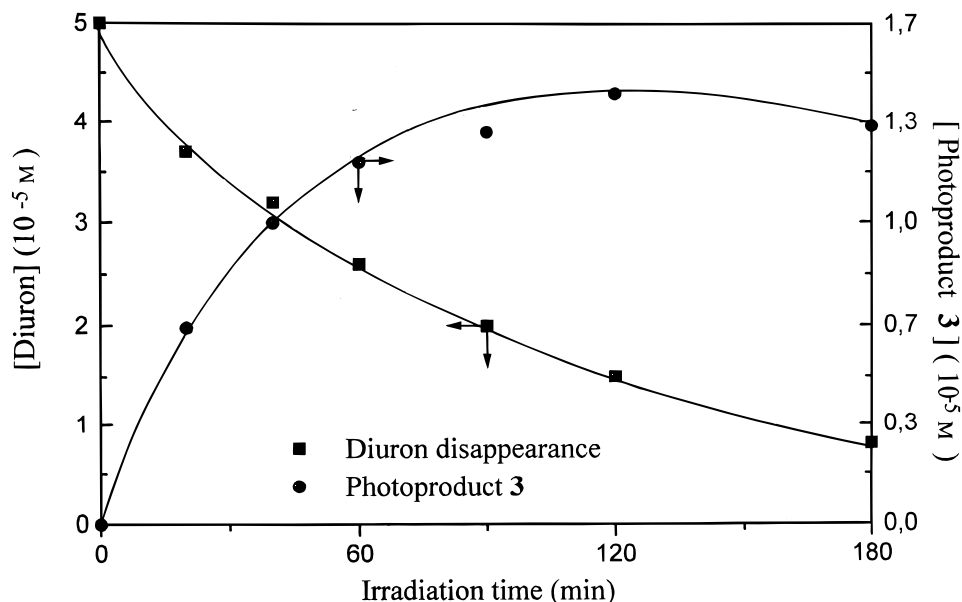


Fig. 7. Kinetics of diuron disappearance and photoproduct 3 formation upon irradiation at 365 nm of a mixture of $[\text{iron(III)}] = 0.20 \text{ mM}$ with 70% of Fe(OH)^{2+} and $[\text{diuron}] = 0.050 \text{ mM}$.

TABLE 4
Nature and Structures of the Photoproducts

Structure	Number	Nature
	1	Primary
	2	Primary
	3	Primary
	4	Primary
	5	Secondary
	6	Secondary

of diuron disappearance.

The mass balance of diuron disappearance was around 75% if we only considered photoproducts 3, 4 and 5. We were not able to quantify the formation of the hydroxylated products. However the overall mass balance of diuron degradation seemed to be near 90%.

3.4 Irradiation under solar light and projection to environment

A mixture of diuron (0.050 mM) and iron(III) (0.20 mM, 70% of monomeric form $\text{Fe}(\text{OH})^{2+}$) was exposed to solar light during a sunny day in July 1995. After 2 h, 90% of the diuron disappeared, and the photoproducts were analogous in nature and percentage to those observed upon excitation at 365 nm. The only difference was the presence of a small amount of dichloroaniline, a product never observed at 365 nm. After 5 h, no more photoproduct was detectable by HPLC (UV detection, $\lambda = 210$ nm); the degradation of diuron and of the aromatic photoproducts was complete.

With an iron(III) solution containing less than 10% of $\text{Fe}(\text{OH})^{2+}$, the rate of diuron degradation strongly decreased, but the reaction was complete after 70 h.

The life-time of diuron when it undergoes the attack

of $\cdot\text{OH}$ radicals coming from excitation of iron(III) aqueous solution was estimated as described by ECETOC.¹⁴ It is based on the experimentally determined 'quantum yield' of diuron disappearance, on the absorption spectrum of iron(III) and on the solar irradiation intensities.

The half life $\tau_{1/2}$ is defined as:

$$\tau_{1/2} = \frac{\ln 2}{2300 \int_{\lambda_1}^{\lambda_2} \phi(\lambda) \cdot I_0(\lambda) \cdot \varepsilon(\lambda) \cdot d\lambda}$$

Where

$\tau_{1/2}$ = half life in s

ϕ = the 'quantum yield' of disappearance of diuron in molecule photon⁻¹ or mol einstein⁻¹ at λ in the range λ_1 – λ_2

I_0 = intensity of sunlight at wavelength λ in einstein cm⁻² s⁻¹ nm⁻¹

ε = molar extinction coefficient at wavelength λ in M⁻¹ cm⁻¹

2300 = a factor taking into account the conversion of litre into cm³ and of decimal units into Napierian logarithms.

The half-lives were calculated using the solar irradiation intensities as presented in the literature.¹⁵ The half-lives were estimated to be around 1–2 h and a few days for solutions containing 70% and less than 10% of monomeric form $\text{Fe}(\text{OH})^{2+}$ respectively. These estimates are in good agreement with our results obtained upon irradiation by solar light in this work.

4 DISCUSSION

Iron(III) species were the only absorbing species when a mixture of diuron and iron(III) in aqueous solution was irradiated at 365 nm. Iron(III) aqueous species are known to undergo a redox reaction giving rise to iron(II) and $\cdot\text{OH}$ radicals, according to eqn (1). Among the iron(III) species present in the solution, $\text{Fe}(\text{OH})^{2+}$ the monomeric form present under our experimental conditions (pH = 3.35) is the most photoreactive one. Accordingly, the rate of diuron photodegradation strongly depends on $\text{Fe}(\text{OH})^{2+}$ concentration at constant iron(III) total concentration. In terms of diuron degradation, the mechanism involves only the attack by $\cdot\text{OH}$ radicals, as evidenced by the total inhibition observed when 2% of isopropanol is added to the solution. The rate of diuron degradation is strongly affected by the excitation wavelength. It increases when λ_{exc} comes down from 365 nm to 313 nm. It is an agreement with the notion that ejection of $\cdot\text{OH}$ radical from the solvent cage requires kinetic energy.⁶

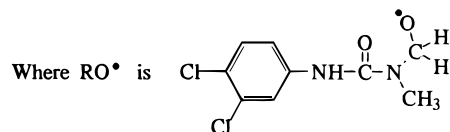
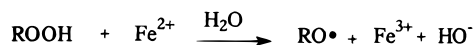
The nature of the photoproducts and more particu-

larly the nature of the major one (3) shows that the attack of $\cdot\text{OH}$ radicals is mainly on the methyl group. This is also true for the photoproduct 4 and even for the secondary photoproducts 5 and 6. The formation of hydroxylated products (attack on the benzene ring) only represents a minor route accounting for a few percent of diuron degradation. From the experimental results, the degradation of diuron photoinduced by iron(III) can be represented as in Fig. 8.

As already mentioned, the first step is the absorption of light by iron(III) species leading to the formation of $\cdot\text{OH}$ radicals. Then two different sites of attack on the molecule are possible:

- On the aromatic ring, with subsequent loss of a chlorine atom and formation of the corresponding hydroxylated photoproducts 1 and 2.

- On the methyl of the dimethylurea group. The alkyl radical $\text{R}\cdot$, formed after the abstraction of a hydrogen atom, reacts with oxygen to form $\text{RO}_2\cdot$ with the subsequent formation of a hydroperoxide by abstraction of a hydrogen atom from diuron. Moreover, it was previously reported that iron(II) catalysed the hydroperoxide decomposition in a Fenton type reaction.¹⁶



$\text{RO}\cdot$ will then undergo two classical β -scissions:¹⁷

- the scission of the C–H bond gives rise to the aldehyde 3.
- the scission of the N–C bond gives rise to the monodemethylated compound 4.

Secondary photoproducts 5 and 6 are rapidly observed. Their formation is possible by a second attack of $\cdot\text{OH}$ radicals on the photoproducts 3 or 4. This accounts for the formation of photoproduct 4 in low yield (less than 5%).

5 CONCLUSIONS

The degradation of diuron photoinduced by iron(III) involves only the attack by $\cdot\text{OH}$ radicals arising from iron(III) species in the excited states. The percentage of monomeric iron(III) species, $\text{Fe}(\text{OH})^{2+}$, appears to be the parameter controlling the rate of diuron degradation: the higher the percentage, the faster the degradation. With respect to the environment, the degradation photoinduced by iron(III) can represent a very efficient way for elimination of diuron that cannot be ignored.

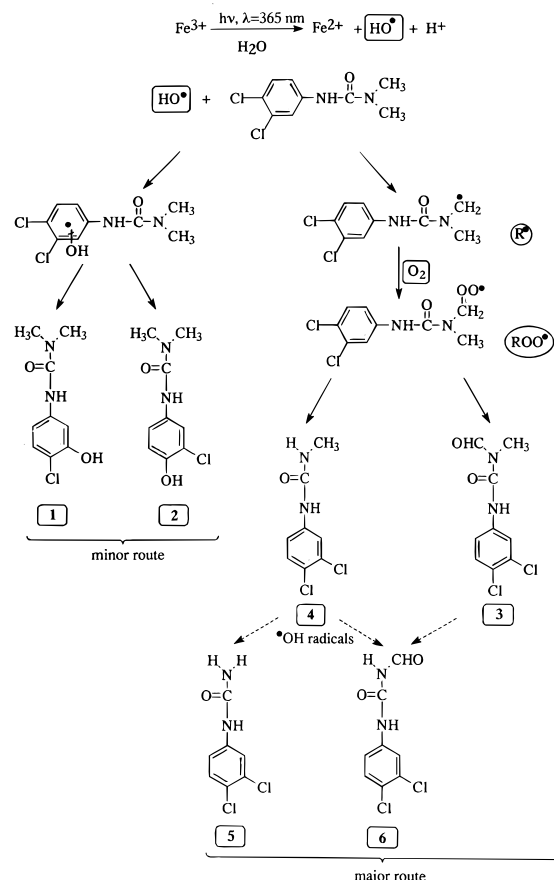


Fig. 8. Routes of photodegradation of diuron induced by iron(III).

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